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54 An oligomerization catalyst, a method for its production and its application

57 A method for the production of an oligomerization catalyst for olefins with between 2 and 6 carbon atoms, in which aluminum oxide is coated with a nickel compound and a sulfur compound, i.e., simultaneously or first with the nickel compound and then with the sulfur compound and the thus obtained catalyst is then dried and calcined, in which case one sets in this manner a molar ratio between sulfur and nickel of between 0.25:1 and 0.38:1 in the finished catalyst.

The catalyst and its use are also described here.

## Description

This invention concerns a method for the production of an oligomerization catalyst for olefins with between 2 and 6 carbon atoms, in which aluminum oxide is coated with a nickel compound and a sulfur compound, i.e., simultaneously or first with the nickel compound and then with the sulfur compound and the thus obtained catalyst is then dried and calcined.

The invention also concerns the thus produced catalysts and a method for the production of oligomers from olefins with between 2 and 6 carbon atoms or from mixtures of these olefins.

Olefins with between 2 and 6 carbon atoms and their mixtures, particularly olefins with 4 carbon atoms, are available in large quantities from FCC-units and also from steam crackers. The respective C<sub>4</sub>-section, i.e., the mixture consisting of butenes and butanes, is very well suited for the production of oligomers and particularly of octenes and dodecenes after the isobutene has been separated. After a hydroformylation and subsequent hydration to form the respective alcohols, octenes as well as dodecenes are used for the production of softening agents or tenside alcohols.

With respect to the use as softening agent alcohol, the degree of branching has a major effect on the softener properties. The degree of branching is described with the ISO-index that indicates the average number of methyl branchings in the respective fraction. For example, n-octene adds 0, methyl heptene adds 1 and dimethyl hexene adds 2 to the ISO-index of a fraction. A lower ISO-index indicates that the molecules in the respective fraction are more linear. The ISO-index gets lower with an increasing linearity and this indicates higher yields in the oxation and better properties for the thus produced softening agents. A lower ISO-index makes softening agents slightly less volatile and PVC shows an improved rupture behavior in a cold environment when it contains such softening agents.

The large-scale oligomerization is performed in a homogeneous- or heterogeneous-catalytic manner.

With respect to the heterogeneous-catalytic working method, aluminum oxide catalysts that contain nickel and sulfur are known already to the prior art. The document JP-B 74/3489 (Nippon Oil Co. Ltd) describes the use of nickel oxide on aluminum oxides as catalyst for the production of low olefin polymers.

Nickel and sulfate are in many cases applied to the carrier in the form of nickel sulfate, in which case the finished catalyst normally has Ni:S ratios around the value 1. Document US-A 2 794 842 (Phillips Petroleum Co.) yields the polymerization of olefins with the use of nickel sulfate on an aluminum oxide carrier. US-A 3 959 400 (Mobil Oil Corp.) presents a method, in which the catalytic dimerization of olefins with between 2 and 4 carbon atoms occurs on aluminum oxides that are coated with nickel sulfate. The document FR-A 2 641 477 (Institut Français du Pétrole) mentions the olefin dimerization with the help of an aluminum oxide that was coated with nickel sulfate. US-A 4 511 750 (Chevron Research Co.) describes the oligomerization of lower olefins with nickel sulfate on a porous inorganic oxide such as aluminum oxide.

Also known are catalysts, in which the Ni:S ratios deviate from the value 1:1. The document US-A 5 883 036 (Koa Oil Co. Ltd) presents the production of aluminum oxide coated with sulfate ions and nickel oxide as catalysts for the oligomerization. The coating with sulfate ions occurs prior to the coating with nickel oxide.

From EP-B 272 970 (Institut Français du Pétrole) is known a method for the dimerization of mono-olefinic hydrocarbons, in which an aluminum oxide with a specific sulfate ion content and with between 0.5 and 15% by weight nickel is used. Furthermore, the molar ratios between sulfur and nickel in the catalyst vary between 0.4:1 and 0.8:1. For the production of this catalyst, the sulfate ion source and the nickel ion source are permitted to act simultaneously upon the aluminum oxide; this is followed by a drying and calcining phase. As an alternative, the aluminum oxide is coated with a nickel salt that decomposes in heat, is dried, calcined and the sulfate ions are applied thereafter.

However, the dimer selectivity and the alkyl chain branching of the olefin oligomers produced with the known catalysts on the basis of aluminum oxides that contain sulfur and nickel are not yet satisfactory.

The task of this invention thus consisted in the presentation of catalysts, with which a higher dimer selectivity and higher degree of linearity of the alkyl groups can be achieved with good olefin yields.

In accordance with the invention, this task was solved by a method for the production of an oligomerization catalyst for olefins with between 2 and 6 carbon atoms, in which aluminum oxide is coated with a nickel compound and a sulfur compound, i.e., simultaneously or first with the nickel compound and then with the sulfur compound, and the thus obtained catalyst is then dried and calcined, in which case one sets in that manner a molar sulfur/ nickel ratio of between 0.25:1 and 0.38:1 in the finished catalyst.

In addition were found the thus available new catalysts and a method for the oligomer production from olefins with between 2 and 6 carbon atoms or a mixture of these olefins.

"Oligomers" include dimers, trimers and higher oligomers of olefins with between 2 and 6 carbon atoms. The process in accordance with the invention is particularly suited for the production of dimers of these olefins.

The catalyst in accordance with the invention can be produced in different ways such as

- a) a co-precipitation from solutions that contain the catalyst components in the dissolved form; the precipitation is washed, dried, formed and calcined (see, for example, DE-A 43 39 713) or
- b) by saturating the aluminum oxide that is present as a powder or already formed with a solution of the nickel and sulfur compound and a subsequent drying and calcining of the obtained product.

One preferably prepares the catalysts in accordance with the invention using method b), i.e., with the use of prefabricated and formed aluminum oxide bodies such as spheres and mainly strands

or star strands with a largest diameter of between 1 and 3 mm. These sizes serve only as examples and do not restrict the object of the presented invention. The aluminum oxide carrier can be obtained in piece-form when the aluminum oxide forerunner or the powder obtained from it through calcining is formed according to the respective requirements and in a generally known manner (see Handbook of Heterogeneous Catalysis, Vol. 1, page 80 and following).

It is known that the chemical and physical properties of the aluminum oxides used for the catalyst production are very much a function of their origin. They are available in a known manner and also commercially. They can be prepared, for example, by calcining aluminum oxide forerunners such as boehmite and hydrargillite.

The catalysts in accordance with the invention are preferably produced with  $\gamma$ -aluminum oxide,  $\eta$ -aluminum oxide as well as their mixtures, i.e., in the form they are commercially available from the companies BASF, Alcoa, Condea, Grace and Rhone-Poulenc. Preference is given to aluminum oxide carriers that mainly and preferably consist completely of  $\gamma$ -aluminum oxide. These aluminum oxides preferably exhibit a water absorption power of more than 0.4 ml/g and a BET surface of more than 150 m<sup>2</sup>/g. Furthermore, preference is given to those aluminum oxides that have a Na<sub>2</sub>O content of less than 0.2% by weight. Preference is also given to aluminum oxides exhibiting an Fe<sub>2</sub>O<sub>3</sub> content of less than 0.2% by weight.

The coating of the aluminum oxide with the nickel compound and the sulfur compound is achieved in a particularly appropriate manner by a saturating with the solutions of these compounds.

For the saturating process, the sulfur compound and the nickel compound are in a preferred manner placed as a solution in water and then in organic polar solvents such as alcohols like methanol and ethanol, or in mixtures of suitable solvents.

Suitable sulfur compounds consist of sulfates and all sulfur compounds that can be converted to sulfate by heating them in the presence of oxygen or of gas mixtures such as air containing oxygen under calcination conditions, such as sulfides. Preference is given to water-soluble sulfates such as ammonium sulfate that decomposes at approx. 250 °C, and particular preference is given to sulfuric acid.

Nickel compounds may consist of any and all nickel compounds that can be converted into an oxidic metal form when they are heated in the presence of oxygen or of gas mixtures like air containing oxygen under calcination conditions. The preferred nickel compound consists of water-soluble nickel salts, for example with an organic anion such as formate, oxalate, acetyl acetate or the 2-ethyl hexanoate and particularly a possibly hydrated nickel nitrate.

During saturation, the aluminum oxide is preferably stirred with a solution that contains precisely those material quantities of nickel compound and sulfur compound with which the aluminum oxide is to be coated. In that regard, the solution volume is preferably selected such that it just equals the water absorption power of the aluminum oxide.

As an alternative, the nickel and sulfur compounds can also be applied in several saturation steps, after which the obtained initial catalyst phase is dried.

When the sulfur compound is to be applied on the aluminum oxide only after the nickel compound was applied in accordance with the invention, it is preferred to previously dry the aluminum oxide coated with the nickel compound at between 50 and 200 °C.

As for the rest, the saturating of the aluminum oxide is achieved in a basically known manner (see, for example, EP-B 272 970).

The saturated catalyst is then dried, i.e., preferably in air and at between 50 and 200 °C.

The calcining is performed in an oxygen-containing atmosphere and preferably in air. The calcination temperature generally varies between 300 and 600 °C. The catalytically effective oxidic active mass that contains nickel and sulfur is formed from the nickel compound and sulfur compound during the calcination phase.

The oligomerization yields undesirable high ISO-values, when the sulfur compound acts first and the nickel compound second upon the aluminum oxide in contrast to the method in accordance with the invention.

Prior to their application, the thus produced new catalysts are during the oligomerization appropriately exposed to a conditioning in a dry nitrogen flow, e.g., at an atmospheric pressure and at temperatures of between 20 and 500 °C and preferably of between 100 and 250 °C to remove traces of moisture (in the air) from the catalyst.

The molar ratio between sulfur and nickel determined with an element analysis in the catalyst in accordance with the invention preferably varies between 0.28:1 and 0.35:1. Above this range, the dimer selectivity and thus generally the catalyst activity normally decreases.

The oligomerization method in accordance with the invention is particularly suited for mixtures of olefins with 3 or 4 carbon atoms. It is particularly well suited for reacting mixtures that contain olefins with 4 carbon atoms, particularly hydrocarbon flows that contain 1-butene and/or 2-butene and are basically free of isobutene, to form dodecenes and particularly octenes. Mixtures with the following composition are suitable hydrocarbon flows with olefins having 4 carbon atoms:

Butane	10 to 90% by weight
Butene	10 to 90% by weight

in which case the butene fraction may have the following composition:

1-butene	1 to 50% by weight
cis-2-butene	1 to 50% by weight
trans-2-butene	1 to 99% by weight
iso-butene	1 to 5% by weight

The so-called Raffinate II is considered a particularly preferred material to be used. This is a C<sub>4</sub>-hydrocarbon mixture that contains butene and is obtained from the C<sub>4</sub>-section from crackers after the separation of higher unsaturated hydrocarbons such as diolefins, particularly 1,3-butadiene, or

acetylene and subsequently the iso-butene contained in it. The following shows a typical composition of Raffinate II:

iso- and n-butane	26% by weight
iso-butene	1% by weight
1-butene	26% by weight
trans-2-butene	31% by weight
cis-2-butene	16% by weight

Butadienes and compounds that contain sulfur and oxygen compounds such as alcohols, aldehydes, ketones or ethers can be removed from the C<sub>4</sub>-hydrocarbon flows through a hydration or adsorption on molecular sieves as indicated in DE-A 39 14 817.

The oligomerization reaction is preferably run at temperatures of between 30 and 140 °C and particularly preferred of between 30 and 120 °C and at a pressure of preferably between 15 and 100 bar and particularly preferred of between 20 and 70 bar. In that regard, the pressure is selected appropriately in such a manner that the hydrocarbon mixture is present in an above-critical manner and particularly in the liquid state at the adjusted temperature. The reactor generally consists of a cylindrical reactor in which the Ni-catalyst is placed and through which the liquid reaction mixture flows, for example, from the top to the bottom. The oligomerization method in accordance with the invention can be run in a single reactor to the desired end of the butene yield, in which case the oligomerization catalyst can be arranged on a single or on several solid beds in the reactor. As an alternative, a reactor cascade consisting of several and preferably of two reactors arranged in series can be used to perform the method in accordance with the invention; when passing the reactor or reactors located upstream of the last cascade reactor, it is possible to run the hydrocarbon oligomerization in the reaction mixture only to a partial conversion level and the desired final conversion level will be achieved only after the reaction mixture has passed through the last cascade reactor. The oligomerization catalyst can be arranged on a single or on several solid catalyst beds in the individual reactors of the reactor cascade. Furthermore, different reaction conditions regarding pressure and/or temperature can be set in the reactors of the reactor cascade within the scope of the above-mentioned pressure and temperature ranges. Although it is preferred to use the same catalyst in all cascade reactors, it is also possible to use different oligomerization products in the individual cascade reactors.

One speaks of a single-stage reaction zone, when a single oligomerization reactor is used or when one uses a reactor cascade, in which the same oligomerization catalyst is used in all reactors.

One speaks of a multi-stage reaction zone, when different oligomerization catalysts are used in the individual cascade reactors.

The oligomerization can be performed under supercritical conditions in relation to the material to be used, in which case it is preferred not to use additional solvents that are not in the supercritical state.

After the formed oligomers have exited the single- or multi-stage reaction zones, the hydrocarbons are separated from them in a generally known manner and all or some of these hydrocarbons are returned in a generally known manner (see, for example, WO-A 95/14647).

The oligomerization method in accordance with the invention can be run in a adiabatic or

isothermal manner.

From a technical point of view, an adiabatic reaction or operation refers to a reaction or operation, in which the whole reaction heat is absorbed by the reaction mixture and is discharged with it from the reactor, i.e., with the exception of the part of the reaction heat that is transferred to the outside through a natural heat conduction and heat dissipation process.

From a technical point of view and in contrast to the above, an isothermal reaction or operation forces the removal of the reaction heat from the reactor with cooling and thermostat devices in a targeted manner and in addition to the natural heat conduction and dissipation process, in which case the reaction heat is generally absorbed first by a heat carrier medium, i.e., the cooling agent, prior to releasing it into the atmosphere or, when heat exchangers are employed, is used to heat substances or to produce energy (see, for example, WO-A 95/14647).

The oligomer separation is achieved in a generally known manner and mainly through a fractionated distillation to particularly form the desired octene and dodecene fractions that serve as initial materials for the hydroformylation to produce the softener alcohols nonanol and tridecanol. Due to the low branching exhibited by the initial oligomers, the higher alcohols produced from them have excellent properties for the production of softening agents and tensides.

## Examples

### I. Catalysts

The  $\gamma$ -aluminum oxide carriers summarized in Table 1 were used for the catalyst production.

The  $\gamma$ -aluminum oxide consisted of the type "D10-10" from the firm BASF or of the type "Pural" from the firm Condea.

Table 1:  $\gamma$ -aluminum oxide carriers used for the catalyst production

Catalyst type*	Form	Water absorption power [ml/g]	Bulk weight [g/l]	Annealing loss [% by weight for 1 h at 900 °C]	BET surface [m <sup>2</sup> /g]
A	1.5 mm strands	0.45	760	7.6	255
B	1.5 mm strands	0.60	661	1.8	280
C	3 mm star strands	0.76	530	1.6	202
D	1.5 mm strands	0.65	661	1.8	280

\* Catalyst designation

General production conditions for the catalysts (the related numbers are shown in the next Table 2).

The  $\text{Ni}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$  used here was manufactured by the firm Fluka.

To manufacture the respective catalysts, the respective carrier was saturated under stirring at room temperature with a solution consisting of the quantities indicated below of 96% H<sub>2</sub>SO<sub>4</sub>, 97% Ni(NO<sub>3</sub>)<sub>2</sub>·6 H<sub>2</sub>O and water. The thus obtained catalyst was dried for 10 hours at 120 °C in air and calcined for 2 hours at 500 °C in air. The percentage content of nickel ("Ni") and of sulfur ("S") in relation to the total weight of the obtained catalyst as well as the sulfur/nickel ratio ("S": "Ni") were then determined.

The sulfur content in the finished catalyst was determined with the quantitative infrared analysis of the sulfur dioxide that formed during the catalyst combustion. The nickel content could be determined by way of the ICP-mass spectrometry.

Table 2: Catalysts EK1 through EK4 in accordance with the invention

No.	Carrier	Carrier quantity [g]	Saturation solution			S [% by weight]	Ni [% by weight]	S : Ni
			H <sub>2</sub> SO <sub>4</sub> [mMol]	Ni (NO <sub>3</sub> ) <sub>2</sub> · 6H <sub>2</sub> O [mMol]	Total solution volume [ml]			
EK1	A	190	92	322	86	1.42	9.08	0.29
EK2	B	200	112	361	115	1.54	9.08	0.31
EK3	C	200	125	361	125	1.67	9.04	0.34
EK4	C	200	132	361	125	1.80	9.02	0.37

Table 3: Reference catalysts VK1 through VK4

No.	Carrier	Carrier quantity [g]	Saturation solution			S [% by weight]	Ni [% by weight]	S : Ni
			H <sub>2</sub> SO <sub>4</sub> [mMol]	Ni (NO <sub>3</sub> ) <sub>2</sub> · 6H <sub>2</sub> O [mMol]	Total solution volume [ml]			
VK1	D	200	83	361	125	1.13	9.10	0.23
VK2	C	200	160	361	125	2.20	9.00	0.45
VK3	D	200	181	361	125	2.38	8.99	0.49
VK4	C	200	230	361	125	3.15	9.00	0.64

#### Reference catalyst VK5 (sulfate applied before the nickel)

A quantity of 380 g of carrier A was saturated under stirring and at room temperature with 171 ml of a solution consisting of 184 mMol H<sub>2</sub>SO<sub>4</sub> (96%) and water. The product was dried in air for 3 hours at 120 °C and calcined for 2 hours in air at 500 °C. The thus obtained catalyst was then saturated under stirring at room temperature with 171 ml of a solution consisting of 644 mMol Ni(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O (97%) and water. The thus obtained catalyst was then dried in air for 2 hours at 120 °C and calcined for 2 hours in air at 500 °C. The percentage content of nickel was then determined as 9.01% by weight and that of sulfur as 1.40% by weight; the molar sulfur/nickel ratio was determined as 0.28.

#### I. Oligomerizations



Raffinate II of the following composition was used for the oligomerization of butene:

29.8% by weight 1-butene  
 31.7% by weight trans-2-butene  
 17.8% by weight cis-2-butene  
 2.1% by weight iso-butene  
 15.3% by weight n-butane  
 3.1% by weight iso-butane  
 0.2% by weight iso-pentane

The reaction was run continuously in a thermostat-controlled tube reactor, whose reaction tube had an inside diameter of 30 mm. The reaction pressure that was higher than the inherent pressure of the Raffinate II was produced with an upstream reactor pump and was controlled downstream of the reactor using commonly known pressure-maintaining devices. A quantity of 1500 NI of dry nitrogen was initially piped hourly across 165 ml of the catalyst for 24 hours at 160 °C in the reaction tube. The reaction tube with the catalyst was then allowed to cool down to 20 °C in nitrogen. At a Raffinate II pressure of 20 bar, the temperature was then increased to 80 °C in 24 hours and the reaction was run under these conditions and at a catalyst load of 3.35 kg Raffinate II per liter catalyst and hour. The reaction discharge was isolated and the percentage content of the isomers with 8 carbon atoms ("C<sub>8</sub>-selectivity") as well as the ISO-index of the C<sub>8</sub>-fraction were determined with the help of a gas chromatography. The results are shown in Table 3.

Table 3

Oligomerization results

No.	Catalyst	S : Ni	Butene yield [% by weight]	C <sub>8</sub> -selectivity [% by weight]	ISO-index
1	EK1	0.29	34	91	1.11
2	EK2	0.31	42	90	1.05
3	EK3	0.34	35	90	1.06
4	EK4	0.37	34	91	1.09
5	VK1	0.23	< 5	Not determined	Not determined
6	VK2	0.45	38	87	1.11
7	VK3	0.49	36	85	1.12
8	VK4	0.64	37	86	1.27
9	VK5*	0.28	28	89	1.25

\* The sulfate was applied before the nickel.

## Patent claims

1. A method for the production of an oligomerization catalyst for olefins with between 2 and 6 carbon atoms, in which aluminum oxide is coated with a nickel compound and a sulfur compound, i.e., simultaneously or first with the nickel compound and then with the sulfur compound and the thus obtained catalyst is then dried and calcined, **characterized by the fact that a molar ratio between sulfur and nickel of between 0.25:1 and 0.38:1 in the finished catalyst is set in this manner.**
2. A method for the production of an oligomerization catalyst for olefins with between 2 and 6 carbon atoms, in which aluminum oxide is simultaneously coated with a nickel compound and a sulfur compound and the thus obtained catalyst is then dried and calcined, characterized by the fact that a molar ratio between sulfur and nickel of between 0.25:1 and 0.38:1 in the finished catalyst is set in this manner.
3. A method for the production of an oligomerization catalyst for olefins with between 2 and 6 carbon atoms, in which aluminum oxide is coated first with a nickel compound and then with a sulfur compound and the thus obtained catalyst is then dried and calcined, characterized by the fact that a molar ratio between sulfur and nickel of between 0.25:1 and 0.38:1 in the finished catalyst is set in this manner.
4. A method in accordance with claims 1 through 3, characterized by the fact that a molar ratio between sulfur and nickel of between 0.28:1 and 0.35:1 in the finished catalyst is set.
5. A method in accordance with claims 1 through 4, characterized by the fact that  $\gamma$ -aluminum oxide or  $\eta$ -aluminum oxide or a mixture thereof is used as the aluminum oxide.
6. A method in accordance with claim 5, characterized by the fact that the aluminum oxide to be used consists of  $\gamma$ -aluminum oxide.
7. An oligomerization catalyst that is available with a method in accordance with claims 1 through 6.
8. A method for the production of oligomers of olefins with between 2 and 6 carbon atoms or of mixtures of these olefins at temperatures of between 20 and 280 °C and at a pressure level of between 10 and 300 bar, characterized by the fact that it is performed in the presence of a catalyst in accordance with claim 7.
9. A method in accordance with claim 8, characterized by the fact that the olefins used in the method have 3 or 4 carbon atoms.
10. A method in accordance with claim 9, characterized by the fact that one uses hydrocarbon flows that contain a mixture of 1-butene and/or 2-butene and butane and that basically contain no isobutene.